

**Liquid-Liquid Equilibria for the Binary Systems Containing  
4-Formylmorpholine (NFM)<sup>1</sup>**

Min Su Ko<sup>2</sup>, Yangjoon Cho<sup>3</sup>, Kyungjin Ha<sup>2</sup> and Hwayong Kim<sup>2,4</sup>

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- <sup>2.</sup> Thermophysical Properties Lab., School of Chemical Engineering Seoul National University Shinlim-dong, Kwanak-ku, Seoul, 151-742, Korea.
- <sup>3.</sup> The 3<sup>rd</sup> Research Lab., Daeduk Research Institute, Honam petrochemical corporation, 24-1 Jang-dong, Yooseong-ku, Taejeon, 305-343, Korea
- <sup>4.</sup> To whom correspondence should be addressed.

## ABSTRACT

Liquid-liquid equilibria (LLE) data were measured for five NFM binary systems with n-Heptane, n-Hexane, Methylcyclohexane, Cyclopentane, and Isohexane at the temperature range of 333.15 K to 408.15 K with a circulation type equipment. The mutual solubility increased as the temperature increased at all these systems. The binary liquid-liquid equilibrium data were correlated with the NRTL and UNIQUAC equations using the parameters which have temperature dependence,  $A_{ij} = a_{ij} + b_{ij} / (T/K-273.15)$ . Both of these two models correlate the experimental data well. The solubility in the NFM increased in the following order at the same temperature; naphthenic hydrocarbons [cyclopentane, methylcyclohexane] and paraffinic hydrocarbons [n-heptane, isohexane, n-hexane].

KEY WORDS: liquid-liquid equilibria; NRTL; n-formylmorpholine; UNIQUAC

## 1. INTRODUCTION

There has been an ever-increasing demand for a higher purity of aromatics as a feedstock for chemical synthesis. Many solvents such as sulfolane (Deal, 1959 [1]; Voetter and Kosters, 1963 [2]; Broughton and Asselin, 1967[3]; Lee and Kim, 1995 and 1998 [4][5]), n-methylpyrrolidone (NMP; Muller, 1973 [6]), glycol (Symoniak, 1981 [7]; Taher and Emina, 1996 [8]), and n-formylmorpholine (NFM; Cinelli, 1972 [9], Mohamed, 1995 [10]) are used to extract the aromatics such as benzene, toluene and xylene from hydrocarbon mixtures.

The NFM extractive distillation process separates aromatics from the reformates. It minimizes aromatic content in gasoline and refines the extracted aromatics, which are used as raw materials of petrochemical processes. This process can recover most of the benzene. The solvent to feed ratio by mass of this process is around 3.5. The operating cost and the initial equipment cost for the overall plant can be reduced by the decision of its optimum value. Commercial process simulators such as PROII (SimSci), HYSYS (Hyprotech) and ASPEN-PLUS (Aspentech) [11] have been used to determine the optimum solvent rate. However, LLE data are not available for these mixtures.

The purpose of this work is to obtain LLE data for each binary system at the operating temperature range of the NFM extractive distillation process. LLE data for the five binary systems were measured at the temperature range from 333.15K to 498.15K, and correlated with the NRTL (Renon and Prausnitz, 1968) [12] and UNIQUAC (Abrams and Prausnitz, 1975) [13] models.

## **2. MEASUREMENT**

### **2.1. Chemicals**

Samsung Chemical Co., Ltd. supplied NFM with a minimum purity of 99.0%. N-heptane was supplied by Kanto Chemical Co., Inc. with a purity of 99.0%. Cyclopentane, n-hexane and isohexane were purchased from Acros AG with 99.0%, 99.0%, and 99.0+% purities, respectively. The minimum purity of methylcyclohexane from JunSei chemical Co., Ltd. was 99.0%. NFM was used after filtration treatment through the 0.45  $\mu\text{m}$  membrane and the rest of the chemicals were used without any purification.

### **2.2. Experimental apparatus**

The sampling parts of the recirculation type apparatus used in the previous studies (Lee and Kim, 1995 and 1998 [4][5]) was modified and used in this study. A schematic diagram of the apparatus is shown in Fig. 1. The system consists of eight major parts: an equilibrium cell, a magnetic pump for circulation, one vapor and two liquid sampling valves, constant temperature air bath, magnetic stirrer, charge-discharge device, temperature and pressure measurement device and an analysis system. The volume of equilibrium cell was  $240\text{cm}^3$ . The cell was made of stainless steel (SUS. 316) and placed inside the air bath. It was controlled by a PID temperature controller to the desired temperature within  $\pm 0.1\text{K}$  (maximum temperature 573K). The cell and the quartz window were sealed with PTFE (Teflon) gaskets. The mixing was promoted by the magnetic stirrer and the magnetic recirculation pumps. Sampling system consists of a sample valve, a sample loop, and a pneumatic actuator. The sample injection valve is a two-position rotary switching valve with an internal sample loop of 1  $\mu\text{l}$ . This is connected with the pneumatic

actuator, which actuates positions. The actuator is operated with a solenoid valve. The vacuum pump was used for discharge of the mixture. The temperature was measured using a 100 $\Omega$ -platinum resistance thermometer of sheath type with a temperature transducer. Its uncertainty was estimated to be within 0.05K. The sampling system were connected to a gas chromatography (Hewlett Packard 5890 Series II) which had a thermal conductivity detector (TCD) and a 6ft  $\times$  1/8in. column packed with Chromosorb WHP 100/120 coated with OV-101. The liquid-phase composition is determined with a maximum relative error of 0.1%.

### **2.3 Experimental Procedure**

The mixture was fed into the equilibrium cell, which was vacuumed in advance. The mixture was stirred for at least 1 hr with a magnetic stirrer and then left to settle for at least 2 hr. The samples were analyzed by GC. The temperatures of the injector and the detector were maintained at 523.15K. After 1 minute holding at 353.15K, the column temperature was raised to the final temperature of 423.15K at the rate of 25 K $\cdot$  min $^{-1}$ . Helium was used as the carrier gas at the rate of 23cm<sup>3</sup> $\cdot$ min $^{-1}$ .

### 3. RESULTS & DISCUSSIONS

The results obtained in this work for five binary systems, n-heptane (1) + NFM (2), n-hexane (1) + NFM (2), methylcyclohexane (1) + NFM (2), Cyclopentane (1) + NFM (2), and isohexane (1) + NFM (2), are presented in Table 1-5, respectively. Concentrations of components,  $i$ , in phase,  $j$ , ( $j=1$ , top phase;  $j=2$ , bottom phase) are given in the mole fraction,  $x_{ij}$ . Effects of the temperature on LLE for the binary systems, NFM and hydrocarbons, are shown in Fig. 2-6. The mutual solubilities of these five binary systems increase as the temperature rises.

NRTL and UNIQUAC models were used to correlate the data for these systems. The value of the nonrandomness parameter,  $\alpha_{ij}$  of NRTL model was fixed at 0.2. NRTL and UNIQUAC interaction parameters were listed in the tables I-V. The temperature dependence of these parameters were fitted to the function

$$A_{ij} = a_{ij} + b_{ij} / (T/K - 273.15),$$

where  $a_{ij}$  and  $b_{ij}$  are constants specific to each system.

Table VI also shows the root mean square deviation (RMSD) defined by

where component,  $i = 1$  and 2, phase,  $j = 1$  and 2, number of data,  $n = 1, 2, 3, \dots, n$ , and  $x$  = liquid mole fraction.

Calculation results of the NRTL and UNIQUAC models were in good agreement with the experimental data. The solubility in the NFM increased in the following order at the same temperature; naphtheneic hydrocarbon [cyclopentane, methylcyclohexane] and paraffinic hydrocarbon [n-heptane, isohexane, n-hexane]. The

results are displayed in Fig. 7.

#### **4. CONCLUSIONS**

Five binary LLE data of hydrocarbon with NFM at 333.15K to 498.15K were determined in this work. The NRTL and UNIQUAC models were useful in correlating the equilibrium data. The temperature dependency of the parameters of NRTL and UNIQUAC models can be expressed as,  $A_{ij} = a_{ij} + b_{ij} / (T/K-273.15)$ .

## **ACKNOWLEDGMENTS**

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Table I. Liquid-Liquid Equilibrium Data and Parameters for the NRTL and UNIQUAC Model for the n-Heptane (1) + NFM (2) Mixture.

Temperature (°C)	Experimental solubility		Parameter			
	of mole fraction		NRTL ( $\alpha=0.2$ )		UNIQUAC	
	Bottom ( $x_{12}$ )	Top ( $x_{11}$ )	$A_{12}$	$A_{21}$	$A_{12}$	$A_{21}$
62.9	0.127482	0.987766	1326.71	215.884	469.248	-67.5823
72.7	0.135131	0.979876	1207.52	234.992	428.677	-56.5174
82.5	0.141728	0.971035	1122.43	257.733	399.28	-46.4905
90.1	0.143181	0.962794	1055.53	287.852	374.938	-35.3053
99.1	0.152760	0.955554	1031.05	292.975	367.556	-33.3723
106.4	0.175513	0.950145	1047.31	258.636	377.481	-44.0762
115.4	0.184426	0.939492	1008.6	274.634	364.227	-38.4463
121.4	0.201241	0.930289	993.933	265.569	361.089	-40.5123
126.1	0.204482	0.921066	957.95	285.349	347.794	-33.541
131.2	0.206204	0.910562	918.35	311.05	332.738	-24.7073
RMSD			1.5946		1.3344	

Table II. Liquid-Liquid Equilibrium Data and Parameters for the NRTL and UNIQUAC Model for the n-Hexane (1) + NFM (2) Mixture.

Temperature (°C)	Experimental		Parameter			
	solubility of mole		NRTL ( $\alpha=0.2$ )		UNIQUAC	
	fraction					
	Bottom ( $x_{12}$ )	Top ( $x_{11}$ )	$A_{12}$	$A_{21}$	$A_{12}$	$A_{21}$
91.6	0.080588	0.981784	1187.84	427.361	356.144	40.9963
100	0.084311	0.965425	982.263	489.066	281.689	76.4414
110.3	0.093454	0.924071	719.68	591.638	185.294	131.719
120.2	0.119234	0.919081	771.632	518.536	209.791	103.899
123.7	0.125697	0.89347	675.363	562.387	173.921	126.564
125.2	0.133549	0.882611	652.222	562.161	166.389	128.619
RMSD			1.7388		1.7920	

Table III. Liquid-Liquid Equilibrium Data and Parameters for the NRTL and UNIQUAC Model for the Methylcyclohexane (1) + NFM (2) Mixture.

Temperature (°C)	Experimental solubility		Parameter			
	of mole fraction		NRTL ( $\alpha=0.2$ )		UNIQUAC	
	Bottom ( $x_{12}$ )	Top ( $x_{11}$ )	$A_{12}$	$A_{21}$	$A_{12}$	$A_{21}$
52.7	0.0612	0.9834	1042.5	462.36	295.677	68.482
62.7	0.069	0.974	943.83	476.69	261.791	81.6341
72.6	0.0768	0.9541	791.17	522.91	206.879	110.073
82.6	0.0875	0.941	747.89	529.21	192.098	116.378
91.8	0.1041	0.9238	707.41	522.26	179.522	118.124
101.2	0.1372	0.9202	775.93	434.37	211.013	83.8326
107.8	0.1575	0.9017	742.52	427.84	200.583	84.8073
RMSD			3.8609		2.7919	

Table IV. Liquid-Liquid Equilibrium Data and Parameters for the NRTL and UNIQUAC Model for the Cyclopentane (1) + NFM (2) Mixture.

Experimental solubility			Parameter			
Temperature	of mole fraction		NRTL ( $\alpha=0.2$ )		UNIQUAC	
(°C)	Bottom ( $x_{12}$ )	Top ( $x_{11}$ )	$A_{12}$	$A_{21}$	$A_{12}$	$A_{21}$
62.7	0.26435	0.98075	1384.78	-21.4047	350.077	10.3146
72.7	0.23677	0.98530	1480.26	4.98817	376.942	14.9457
82.2	0.22000	0.98447	1476.13	38.4987	368.807	31.2165
92.1	0.20387	0.95413	1086.47	177.095	222.397	124.926
101.8	0.24179	0.88569	804.923	270.736	122.737	192.915
111.8	0.30635	0.78724	642.817	334.25	66.5787	236.702
116.6	0.35332	0.72926	597.976	349.055	51.0151	248.199
121.6	0.42826	0.65775	582.609	342.308	45.1772	248.661
RMSD			7.1665		6.4267	

Table V. Liquid-Liquid Equilibrium Data and Parameters for the NRTL and UNIQUAC Model for the Isohexane (1) + NFM (2) Mixture.

Temperature (°C)	Experimental solubility		Parameter			
	of mole fraction		NRTL ( $\alpha=0.2$ )		UNIQUAC	
	Bottom ( $x_{12}$ )	Top ( $x_{11}$ )	$A_{12}$	$A_{21}$	$A_{12}$	$A_{21}$
80.2	0.0789	0.996552	1728.69	349.271	543.957	-21.5953
92	0.083011	0.987543	1334.33	389.194	408.817	18.818
101.5	0.108193	0.962071	1008.2	408.088	298.642	49.9631
110.7	0.11483	0.952098	955.15	428.24	279.114	60.5441
120.5	0.134133	0.9324	879.12	433.927	253.538	68.6554
RMSD			2.8390		3.0923	

Table VI. Optimum Interaction Parameters According to the Equation  $A_{ij} = a_{ij} + b_{ij} / (T/K-273.15)$

Binary System	$A_{12}$	NRTL		UNIQUAC	
	$A_{21}$	$a_{ij}$	$b_{ij}$	$a_{ij}$	$b_{ij}$
n-heptane (1)	$A_{12}$	-146.11	442482	-23.224	148338
+ NFM (2)	$A_{21}$	353.11	-27296	46.497	-31873
n-hexane (1)	$A_{12}$	-4667.53	2114758.84	-1708.87	745198.02
+ NFM (2)	$A_{21}$	1824.20	-499557.30	976.70	-336622.38
methylcyclohexane (1)	$A_{12}$	-2195.22	1053890.33	-833.59	367620
+ NFM (2)	$A_{21}$	1108.34	-210634.86	569.78	-163356
cyclopentane (1)	$A_{12}$	-5327.35	2326165.24	-2166.93	869381.16
+ NFM (2)	$A_{21}$	2823.4	-968182	1895.19	-645114.06
isohexane (1)	$A_{12}$	-6783.48	2975560.47	-2365.91	1017206.98
+ NFM (2)	$A_{21}$	1195.32	-296478.26	884.08	-317110.33

Fig. 1. A schematic diagram of the apparatus for LLE experiments


Fig. 2. Experimental and calculated liquid-liquid equilibrium data for the n-heptane (1) + NFM (2) mixture. Point, experimental results: , solid line: NRTL with  $\alpha = 0.2$ , dot line: UNIQUAC.


Fig. 3. Experimental and calculated liquid-liquid equilibrium data for the n-hexane (1) + NFM (2) Mixture. Point, experimental results: , solid line: NRTL with  $\alpha = 0.2$ , dot line: UNIQUAC.


Fig. 4. Experimental and calculated liquid-liquid equilibrium data for the methylcyclohexane (1) + NFM (2) Mixture. Point, experimental results: , solid line: NRTL with  $\alpha = 0.2$ , dot line: UNIQUAC.


Fig. 5. Experimental and calculated liquid-liquid equilibrium data for the cyclopentane (1) + NFM (2) Mixture. Point, experimental results: , solid line: NRTL with  $\alpha = 0.2$ , dot line: UNIQUAC.


Fig. 6. Experimental and calculated liquid-liquid equilibrium data for the isohexane (1) + NFM (2) Mixture, Point, experimental results: , solid line: NRTL with  $\alpha = 0.2$ , dot line: UNIQUAC.

Fig 7. Mutual solubility for the NFM and nonaromatic mixture.

